

22.07.03

power of attorney

Patent Cooperation Treaty

Appointment of Agent

REC'D 13 AUG 2003

WIPO

PCT

The undersigned applicant(s) hereby appoint(s) as agent

van Westenbrugge, Andries; Jorritsma, Ruurd; de Bruijn, Leendert C.; Plaisier, Aart; Janssen, F.H.J.F.; Kraag F.; Coppens, J.H.M.; Baarslag, A.D.; Wiegerink, Franciscus J.; de Vries, Erik E.; Bottema, Hans J.; Hutter, Jacobus Johannes; Groeneveld, Yme G.; KETELAARS, Maarten F.J.M.; SWINKELS, Bart Willem; BOT, David Simon Maria, RINGELING, Patricia Louise, DE ZEEUW, Rick, DE BOER, H.J.R. of Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, 2502 LS THE HAGUE, the Netherlands

to act on his (her, their) behalf before the competent International Authorities in connection with the international application concerning:

Process for cleaning filters

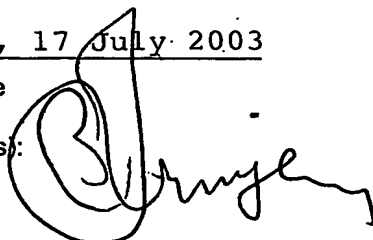
and to receive payment on their behalf.

agent's file reference: P045320PCT

Delft, 17 July 2003

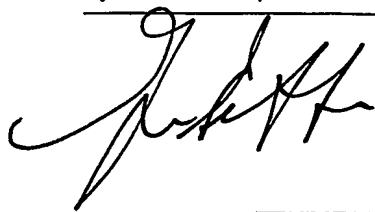
place, date

signature(s):

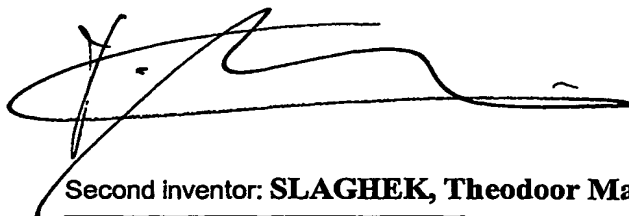


Applicant: **Nederlandse Organisatie voor Toegepast-Natuurwetenschappelijk Onderzoek TNO**

by: KRULJEN, Bert (Director)



First inventor: **JETTEN, Jan Matthijs**



Second inventor: **SLAGHEK, Theodoor Maximiliaan**

**PRIORITY
DOCUMENT**

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)



**Europäisches
Patentamt**

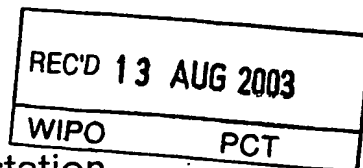
**European
Patent Office**

PCT/NL

03 / 0046

**Office européen
des brevets**

22.07.03



Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02077580.5

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr.:
Application no.: 02077580.5
Demande no:

Anmeldetag:
Date of filing: 28.06.02.
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

NEDERLANDSE ORGANISATIE VOOR
TOEGEPAST-NATUURWETENSCHAPPELIJK ONDERZOEK
TNO
Schoemakerstraat 97, P.O. Box 60680
2628 VK Delft
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Process for cleaning filters

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s)
revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

B01D65/00

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR

28.06.2002

Process for cleaning filters

(99)

5 [0001] The invention relates to a process of cleaning food processing equipment, in particular membrane filters which are used for producing liquid foodstuffs, wherein the filters are contacted with an oxidator.

10 [0002] In the food industry, use is being made to an increasing extent of membrane filters, in particular plastic membranes such as polyvinylpyrrolidone, polysulphone, polyether-sulphone and certain types of polyamides, and ceramic membranes for removing undesirable insoluble matter from beverages and other liquids. Such membranes are also used for cleaning surface water. Such membranes ensure an expedient removal of undesirable constituents, in particular micro-organisms such as algae, fungi, yeast, and bacteria.

15 [0003] The problem is, however, that such membrane filters become blocked even after a short time so that they become unusable. The blocked filters can be regenerated, for example by rinsing them through in the opposite direction. However, that is a complicated process and no longer effective in the long term because the contamination accumulates. In addition, it is difficult to remove some persistent organic contaminants in this way.

20 [0004] WO 97/45523 describes the use of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) as nitroxyl compound and hypochlorite and hypobromite as a reoxidator for cleaning beer-settling modules. The presence of halogen residues, especially bromine residues, is highly undesired in equipment used for preparing or treating beverages and other foodstuffs. Moreover, the amounts of oxidator and reoxidator used are high and therefore this method is relatively expensive.

[0005] WO 99/15256 discloses the use of cyclic nitroxyl compounds such as TEMPO together with a calcium-sequestering agent for cleaning filters to be used in purifying surface water. This method is not very effective for cleaning filters with heavy residues produced in the beverage industry.

30 [0006] US 5,647,988 and JP-A 9-290141 disclose a method for cleaning ceramic membranes used in water-purification plants and the like, by using a back-washing method in combination with an oxidising agent such as sodium hypochlorite, chlorine and chlorine dioxide followed by a washing with a reducing agent.

[0007] Research has revealed that during the membrane separation process for cleaning foodstuffs such as beer, the membrane fouling starts with a complexation onto the membrane consisting of a complex of polyphenols and proteins. Subsequently other components such as (poly)saccharides and/or other hydrophilic residues of e.g. yeast adsorb onto the polyphenol protein complex and as a result the pores of the membranes are blocked. The blocking of the membrane pores results in reduced permeability and ultimately in an inefficient filtration process.

[0008] In order to clean the used membranes, it was surprisingly found that filters and other equipment used in the food and beverage industry can be effectively cleaned in a TEMPO-free process. The cleaning process is focused on targeting the polyphenol protein complex with an oxidising chemical aid such as sodium hypochlorite, Oxone, organic peracids or a transition metal complex together with peroxide compounds such as hydrogen peroxide, or oxidising enzymes. In all cases it is not necessary that after the oxidative cleaning the membranes have to be treated with a reducing agent. The research has resulted in two methods, which are feasible for cleaning the membranes. The two methods have in common, as the inventive concept, that the protein and/or polyphenol containing residues are treated with the oxidising agent capable of oxidising the proteins and/or polyphenols, while minimising contact of the oxidising agent with the polysaccharides. The reduced contact with oxidising agent has the further advantage that the life cycle of the membranes is increased.

[0009] The first method is focused on a two step circular cleaning sequence whereby first the carbohydrates or other hydrophilic residues, which are attached onto the polyphenol protein complex, are treated with an alkaline solution, in particular at pH 11-14, especially 12-13. This treatment is followed by an oxidative chemical or enzymatic treatment. The alkaline treatment is necessary for (partial) solubilisation of the (poly)-carbohydrates, resulting in a better access to the polyphenol protein complex; without oxidising agent being spent by oxidising the polysaccharides and other oxidisable, alkali-soluble material. The polyphenol-protein complex is subsequently removed by typical oxidative chemical aids such as sodium hypochlorite, organic and inorganic peracids and the like or via an enzyme-induced oxidation using oxidizing enzymes. Examples of oxidising enzymes (oxidoreductases) include peroxidases and oxidases, in particular polyphenol oxidases and laccase, such as Suberase® and *Trametes versicolor* laccase, in combination with oxygen.

[0010] The cleaning chemicals such as hypochlorite are used in a concentration of between 1 and 1000 ppm, especially between 30 and 600 ppm. Depending on the type of cleaning agent the pH varies between 3 and 11. The cleaning temperature may be between 4 and 80 °C, preferably between 15 and 60 °C, most preferably between 20 and 50 °C. After the cleaning sequence the membranes are rinsed before use. In case of the enzyme treatment the enzyme is used in concentrations between 1 and 10000 ppm, preferably between 20 and 7000 ppm, and most preferably between 50 and 5000 ppm. Further conditions are a pH range between 5 and 8 at temperatures between 20 and 80 °C, preferably between 30 and 70 °C. During the cleaning sequence air is bubbled through the solution but pure oxygen is also feasible. Additional buffers, e.g. succinate buffers can be used for stabilisation purposes.

[0011] The second method uses a back-wash step. Since research has revealed that the polyphenol protein complex is directly attached through physical bonds to the membrane surface, surprisingly it is possible to target the polyphenol protein complex directly using typical oxidative chemicals such as sodium hypochlorite, organic and inorganic peracids and the like. The cleaning chemicals are used in a concentration of between 1 and 1000 ppm, especially between 30 and 600 ppm. Depending on the type of cleaning aid the pH may vary between 3 and 11. The cleaning temperature may be between 4 and 80 °C, preferably between 15 and 60 °C, most preferably between 20 and 50 °C. In case of the enzyme treatment the enzyme is used in concentrations between 1 and 10000 ppm, preferably between 20 and 7000 ppm, and most preferably between 50 and 5000 ppm. Further conditions are a pH range between 5 and 8 at temperatures between 20 and 80 °C, preferably between 30 and 70 °C. During the cleaning sequence air is bubbled through the solution but pure oxygen is also feasible. Succinate or other buffers can be used for stabilisation purposes. For cleaning using a back-wash, it is preferred to use a back-wash flux of between 0,5 and 100 l of cleaning solution per h per m² per h for a period of time between 1 and 100 min, depending on the degree of fouling of the membrane.

[0012] After the cleaning process, using one the above described methods, the filters are preferably rinsed with water several times before use. It is not necessary to use of a reducing agent after the oxidative treatment in the process of the invention.

[0013] The peracid described may be any peralkanoic acid such as peracetic acid, perpropionic acid, perlauric acid etc., a substituted alkanoic acid such as peroxy-

trifluoroacetic acid, an optionally substituted aromatic peracid such as perbenzoic acid or m-chloroperbenzoic acid, or an inorganic peracid such as persulphuric acid or permanganic acid. The peracids may be formed in situ from a precursor such as the corresponding aldehyde, (carboxylic) acid, acid anhydride, ester or amide, e.g. tetra-
5 acetyl-ethylenediamine (TAED), with a suitable halogen-free oxidising agent, such as hydrogen peroxide or oxygen, either before the oxidation reaction or during the oxidation reaction, or with perborates or percarbonates or the like, in the presence of acylating agents such as TAED. The peracids may be used as such, or in the form of a suitable salt, especially an alkali metal salt. A suitable form of persulphuric acid is e.g.
10 Oxone® ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), which is commercially available.

[0014] The transition metal oxidator can be a combination of a transition metal, such as iron, manganese, chromium, cobalt or vanadium, with a hydroperoxide, such as t-butyl hydroperoxide or another alkyl hydroperoxide, or, preferably hydrogen peroxide or oxygen. The preferred transition metals are iron and, especially, manganese. The
15 transition metal is preferably in the form of a complex with a nitrogen-containing organic compound, preferably containing at least two nitrogen atoms such as ethylenediamine, diethylenetriamine, triazacyclononane and their N-methylated analogues, bipyridyl and the like.

[0015] For the back-wash method, the preferred oxidising agents include peracids such as
20 Oxone, transition metal complexes with hydrogen peroxide, and enzymes such as laccase.

[0016] It was found surprisingly that treatment of membrane filters using either of the two described methods results in a cleaning performance which is equal to or better than that of treatment with hypochlorite/bromide in combination with TEMPO as described in WO 97/45523. Also the amount of cleaning chemical necessary for cleaning the
25 membranes can be severely reduced compared to method described in WO 97/45523 since the cleaning chemical is only used to remove the polyphenol protein complex. The limited use of the chemical aid also is beneficial for the stability of the membranes used. As an example, the amount of oxidising agent to be used for cleaning membrane filters according to either one of the processes of the invention is between 100 and 2500 mg of
30 oxidising agent (hypochlorite) per 1000 l of beer produced, whereas the process of WO 97/45523 requires about 4500 mg of hypochlorite and additional TEMPO per 1000 l of the same type of beer. Similar improvements can be achieved for filter membranes used in the production of fruit juices and the like.

[0017] The process of the invention may be used for cleaning filters used in food industry and in feed industry. Such equipment may especially be used in the production of dairy products, beer, wine, fruit juices (apple, pineapple, grape, grapefruit, orange, lemon, etc.), vegetable juices and other beverages and liquids used in food processing.

5 Suitable examples of such equipment include pipes, tubes, capillaries, mixing devices and, in particular, filters. The filter may be of any type, including polymer membranes wherein the polymer may be polyvinylpyrrolidone, polysulphone, polyether-sulphone and especially polyamides, and ceramic membranes made of e.g. silica, aluminium oxide etc.

10 [0018] The process of the invention may proceed by solubilisation of carbohydrates and oxidation and/or solubilisation other high molecular weight biomolecules proteinaceous materials, polyphenolic compounds, in residues to be removed from the filters. Such cleaning procedures are preferably carried out by treating the equipment with an aqueous solution of the chemical aid. The process of the invention can be performed as
15 a static process, i.e. batch-wise treatment of the equipment in a suitable container containing the treatment liquid for a period of between several seconds and several hours, especially between 3 minutes and 1 hour. The process can also be a dynamic process, i.e. a process wherein a continuous or semi-continuous flow of the treatment liquid is passed over or through the equipment, e.g. at a rate of 5 ml to 10 l per minute,
20 depending on the size of the equipment. After the cleaning sequence, the equipment is rinsed with rinsing liquid, which can be water or a neutralising aqueous liquid or an organic solvent such as an alcohol solution, or a mixture or sequential combination thereof.

Example 1: *Cleaning filters using hypochlorite and the circular method*

25 [0019] A filtration membrane (hollow tube containing 40 membrane hollow fibres, pore size 0.5 micron) with a total surface area of 0.04 m² (resembling the X-flow R-100 modules used in large scale facilities) was used for filtering beer. The membranes were fouled using a dead-end filtration technique until the pores were blocked resulting in minimal permeate or flux. A solution of sodium hydroxide at pH 13 was used to partly
30 solubilise the polymeric carbohydrates. After 10 minutes a solution of 100 ppm of hypochlorite was used for 10 to 30 minutes to clean the membranes. Then the pH was adjusted to 7. The cold water flux (cwf) of the virginal membrane was 6000 l/h/m². The cwf after cleaning was also 6000 l/h/m².

Example 2: *Cleaning filters using peroxosulphuric acid and the circular method*

[0020] Membranes were fouled and treated with alkaline solution at pH 13 as in Example 1. After 10 minutes a solution containing 100 ppm of peroxosulphuric acid was used for 10 to 30 minutes to clean the membranes as in Example 1. The reaction pH was adjusted to 7. The cold water flux (cwf) of the virginal membrane was 6000 l/h/m². The cwf after cleaning was also 6000 l/h/m².

Example 3: *Cleaning filters using a manganese complex/hydrogen peroxide and the circular method*

[0021] Membranes as fouled according to Example 1 were cleaned. The cleaning sequence started with a pretreatment of flushing the membranes with alkaline at pH 13. After 10 minutes a solution containing 2000 ppm of hydrogen peroxide (or 2000 ppm peracetic acid) and 50 ppm of an Mn complex with 1,4,7-trimethyl-1,4,7-triazonane for half an hour was used to clean the membranes. The reaction pH was adjusted to 10. The cold water flux (cwf) of the virginal membrane was 6000 l/h/m². The cwf after cleaning was also 6000 l/h/m².

Example 4: *Cleaning filters using enzymes and the circular method*

[0022] Membranes were fouled and treated with alkaline solution at pH 13 as in Example 1. After 10 minutes the pH was brought to 6 and a laccase solution was added resulting in a 500 ppm concentration. Once the flux through the membrane unit is comparable to the virgin flux the solution is removed and the membrane unit is rinsed with water.

Example 5: *Cleaning filters using peroxosulphuric acid and the back-flush method*

[0023] Membranes as fouled according to Example 1 were cleaned. The flux direction is opposite to the filtrate direction. The membranes are cleaned with a solution containing 100 ppm peroxosulphuric acid. Once the flux through the membrane unit is comparable to the virgin flux the solution is removed and the membrane unit is rinsed with water.

Example 6: *Cleaning filters using a manganese complex/hydrogen peroxide and the back-flush method*

30 Membranes as fouled according to Example 1 were cleaned. The flux direction is opposite to the filtrate direction. The membranes are cleaned with a solution containing

2000 ppm of hydrogen peroxide (or 2000 ppm peracetic acid) and 50 ppm of an Mn complex with 1,4,7-trimethyl-1,4,7-triazonane. Once the flux through the membrane unit is comparable to the virgin flux the solution is removed and the membrane unit is rinsed with water.

5 **Example 7: *Cleaning filters using enzymes and the back-flush method***

Membranes as fouled according to Example 1 were cleaned. The flux direction is opposite to the filtrate direction. The membranes are cleaned using a solution containing 500 ppm laccase. Once the flux through the membrane unit is close to virgin levels the membrane unit is rinsed with water resulting in a flux comparable to virgin levels.

Claims

(99)

1. A process of cleaning a filter containing residues from filtering beverages, the residues comprising water-insoluble proteins and/or polyphenols attached to the filter and polysaccharides, comprising contacting the protein and/or polyphenol containing residues with a solution containing an oxidising agent capable of oxidising proteins and/or polyphenols and while minimising contact of the oxidising agent with the polysaccharides.
2. A process according to claim 1, wherein the oxidising agent is a hypohalite, a peracid, or a peroxide compounds together with a transition metal.
3. A process according to claim 1, wherein the oxidising agent is an enzyme.
4. A process according to claim 1 or 2, wherein the solution containing the oxidising agent has a pH between 3 and 11.
5. A process according to any one of claims 1-4, wherein the filter, prior to contacting with the solution of the oxidising agent, is contacted with an alkaline solution.
6. A process according to claim 5, wherein the alkaline solution has a pH between 11 and 14.
7. A process according to any one of claims 1-4, wherein contacting with the solution of the oxidising agent is performed as a back-flush.
8. A process according to claim 7, wherein the back flush is performed at a rate of 0,5 - 100 l of the solution per h per m² of filter surface.

28.06.2002

99

Abstract

Filters used in the beverage industry fouled by polyphenol-protein complexes and carbohydrate polymers can be cleaned by treating the filters either with the following methods:

- 1) Solubilisation of at least part of the carbohydrate polymers followed by a treatment of the resulting polyphenol protein complex with an oxidative chemical or enzyme.
- 2) Treatment of the fouled filters through a back-wash method using an oxidative chemical or enzyme.

In both cases it is not necessary to rinse the membranes after cleaning with a reductive chemical.